

D E C L A R A T I O N

I, Koichi NAKA of 19-16, Daiwanishi 2-chome,
Kawanishi-shi, Hyogo 666-0112 Japan hereby declare that I
am conversant with the Japanese language and that I am the
translator of the document attached and certify that to the
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Koichi NAKA

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(Translation)

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[INVENTOR]
[DOMICILE OR RESIDENCE] 832-13, Kozato, Ueda-shi, Nagano
[NAME] Yoshio TAKASU

[INVENTOR]
[DOMICILE OR RESIDENCE] 2-24-10, Chuo, Ueda-shi, Nagano
[NAME] Yasushi MURAKAMI

[INVENTOR]
[DOMICILE OR RESIDENCE] 124-2, Nakanojo, Ueda-shi, Nagano
[NAME] Wataru SUGIMOTO

[PATENT APPLICANT]
[DOMICILE OR RESIDENCE] 124-2, Nakanojo, Ueda-shi, Nagano
[NAME OR CORPORATE NAME] Wataru SUGIMOTO

[ATTORNEY]
[ID NUMBER] 100072431
[PATENT ATTORNEY]
[NAME OR CORPORATE NAME] Kazuo ISHII

[SELECTED ATTORNEY]
[ID NUMBER] 100117972
[PATENT ATTORNEY]
[NAME OR CORPORATE NAME] Shinichi KAWASAKI

[INDICATION OF OFFICIAL CHARGE]**[NUMBER IN PRE-PAYMENT REGISTER]** 066936**[AMOUNT PAID]** ¥21,000**[LIST OF DOCUMENTS SUBMITTED]****[TITLE OF DOCUMENT]** Specification 1**[TITLE OF DOCUMENT]** Drawing 1**[TITLE OF DOCUMENT]** Abstract 1**[NECESSARY OR NOT OF PROOF]** Necessary

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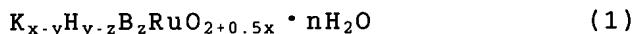
[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION] LAYERED RUTHENIC ACID COMPOUND,
PRODUCTION METHOD THEREOF AND ELECTRODE FOR ELECTROCHEMICAL
DEVICE USING THE SAME

[CLAIMS]

[Claim 1] A layered ruthenic acid compound characterized by having high diffraction intensities at (001), (002), (003) and (004) planes, respectively, and having a layered crystalline structure with a thickness of 1 nm or smaller.

[Claim 2] A layered ruthenic acid compound represented by the formula (1)



[where B is alkylammonium represented by $(R)_mNH_{4-m}$ or $(R)_{m-n}(R')_nNH_{4-m}$ (where R and R' are $CH_3(CH_2)_p$, m = 0 to 4, n = 0 to 3, p = 0 to 18), $0 < x < 1$, $0 \leq y < x$, $0 \leq z < y$, $0 \leq n \leq 10$].

[Claim 3] A method of producing a layered potassium ruthenate characterized by heating ruthenium oxide and a potassium salt at 700-900 °C.

[Claim 4] A method of producing a layered potassium ruthenate characterized by melting ruthenium oxide and potassium hydroxide at 500-700 °C.

[Claim 5] A method of producing a protonic layered ruthenic acid hydrate characterized by treating a layered potassium ruthenate in an acidic solution.

[Claim 6] A method of producing a layered alkylammonium-ruthenic acid intercalation compound characterized by reacting a protonic layered ruthenic acid hydrate with alkylammonium represented by $(R)_mNH_{4-m}$ or $(R)_{m-n}(R')_nNH_{4-m}$ (where R and R' are $CH_3(CH_2)_p$, m = 0 to 4, n = 0 to 3, p = 0 to 18).

[Claim 7] A method of producing a layered alkylammonium-ruthenic acid intercalation compound characterized by reacting a protonic layered ruthenic acid hydrate with alkylamine represented by $(R)_mNH_{3-m}$ or $(R)_{m-n}(R')_nNH_{3-m}$ (where R and R' are $CH_3(CH_2)_p$, m = 0 to 3, n = 0 to 2, p = 0 to 18).

[Claim 8] An electrode for an electrochemical device containing the layered ruthenic acid compound according to claim 1 or 2.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a novel ruthenic acid compound, a production method thereof and an electrode for an electrochemical device using the ruthenic acid compound.

[0002]

[Prior Art]

So far, there are typical examples of an electrochemical device having power storage capability such as electrical double-layer capacitors, electrochemical capacitors, secondary batteries and memory devices. These devices have been applied to practical equipment while taking advantage of their characteristics.

Due to its higher power density and longer life than the secondary battery, the electrical double-layer capacitor has been used in backup power sources requiring high reliability. On the other hand, the secondary battery, which is higher in energy density than the electrical double-layer capacitor, is the most typical and classic power storage device. However, the secondary battery is shorter in life than the electrical double-layer capacitor and has to be replaced with a new one after a certain use period. On the other hand, the memory device has already been commercialized as a reusable timer, but development of a long-term timer running for 10 to 15 years has been waited for.

[0003]

Characteristic differences among these power storage devices are mainly dependent on their mechanisms for storing electric power.

The electrochemical capacitor generates a capacitance by electrochemical adsorption at an interface between the surface of rutile-type oxide of metal such as RuO₂, IrO₂ or Co₃O₄ and an electrolyte. This capacitance is called pseudo-

capacitance and distinguished from an electrical double-layer capacitance generated at an interface between the surface of an activated carbon electrode and an electrolyte. Thus, the electrochemical capacitor does not cause an electrochemical reaction at the interface between the electrode and the electrolyte, but only brings about movement of ions contained in the electrolyte during charge/discharge. Accordingly, the capacitor is not as easily deteriorated as the secondary battery, permitting long life and high power density due to the movement of ions at high speed.

[0004]

On the other hand, the secondary battery is apt to deteriorate easily through charge/discharge because it utilizes the electrochemical reaction between the electrode and the electrolyte. The chemical reaction speed is relatively low, resulting in short battery life and relatively low power density. However, since the electrode material itself stores the energy in the form of chemical energy, the secondary battery shows higher energy density than the electrical double-layer capacitor that stores the energy only at the interface between the electrode and the electrolyte.

[0005]

In view of these conventional power storage devices, there has been proposed an electrochemical capacitor having high power density and long life, which are characteristics of the electrical double-layer capacitor, and high energy density,

which is a characteristic of the secondary battery. Typical electrode materials of the electrochemical capacitor are ruthenium, iridium and cobalt. However, since each of these materials is expensive, reduction in cost and increase in performance have been challenges to be solved.

[0006]

As solutions to the challenges, there have been proposed an electrode dispersing rutile-type RuO₂ therein, an electrode material comprising a ruthenium compound and a vanadium compound adsorbed on activated carbon (see Patent Publication 1) and a method of forming an electrode containing a solid solution of a ruthenium compound and a vanadium compound.

[0007]

[Patent Publication 1]

Japanese Laid-Open Patent Publication No. HEI11-354389

[0008]

[Problem That the Invention Is to Solve]

If a ruthenium compound, which is expensive, is supported on the surface of a host material such as activated carbon, the ruthenium compound will have a rutile-type or amorphous crystal structure. Accordingly, the initial voltage is expected to be high, but the ruthenium compound may come off the host material through repetitive charge/discharge for a long time. Further, if a vanadium compound is added, bond strength to the host material decreases, causing dropping of

the ruthenium compound through the long-term charge/discharge. Thus, a problem of battery life remains to be solved.

[0009]

So far, a layered compound such as graphite has received attention as an electrode material. Typically used layered compounds are graphitizable carbon, TiS_2 , MoS_2 , CoO_2 and V_6O_{13} , whereas the synthesis of a layered ruthenium compound has been difficult.

The present invention intends to provide a novel layered ruthenic acid compound having an increased active area and significantly improved charging capability.

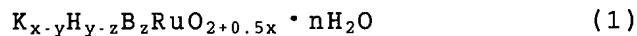
Further, the present invention intends to provide an electrode capable of realizing a high-powered large-capacitance electrochemical capacitor by using the layered ruthenic acid compound.

[0010]

[Means for Solving the Problem]

A layered ruthenic acid compound according to the present invention is characterized by having high diffraction intensities at (001), (002), (003) and (004) planes, respectively, and having a layered crystalline structure with a thickness of 1 nm or smaller.

The present invention provides a layered ruthenic acid compound represented by the formula (1)



[where B is alkylammonium represented by $(R)_mNH_{4-m}$ or

(R)_{m-n}(R')_nNH_{4-m} (where R and R' are CH₃(CH₂)_p, m = 0 to 4, n = 0 to 3, p = 0 to 18), 0 < x < 1, 0 ≤ y < x, 0 ≤ z < y, 0 ≤ n ≤ 10].

[0011]

[Mode for Embodying the Invention]

The inventors of the present invention have succeeded in synthesizing a compound comprising a stacked structure having a thickness of 1 nm or smaller and in making the compound into fine particles (an increase in area) by adding potassium salt to a ruthenic compound. Further, it has been found that these layered compounds, if combined with carbon as a host material or given with proton conductivity, allow an improvement in properties of an electrochemical capacitor by about 10 times larger than that of a conventional one.

The present invention is based on the results of a study intended to allow easy movement of protons in a solid bulk of a layered ruthenium oxide in which a crystal structure of crystalline ruthenium oxide and water layers are separated on the nanometer level. The layered ruthenium oxide of the present invention includes electron conductive layers comprising sheet-like ruthenium oxide crystals of the nanometer level having electrochemical stability (hereinafter referred to as nanosheets) and proton conductive layers comprising water or hydrated proton. Owing to the layered structure of the electron conductive layers and the proton conductive layers on the molecular level, the charging

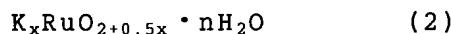
capability of the crystalline ruthenium oxide is allowed to increase significantly. The crystalline ruthenium oxide is a useful material for a high-powered large-capacitance supercapacitor.

[0012]

The layered ruthenic acid compound of the present invention has high diffraction peak intensities at a (001) plane ($l = 1$ to 4) having a plane index of (hkl) . In particular, the layered ruthenic acid compound is characterized in that the diffraction peak intensities at (001) and (002) planes are higher than those at (003) and (004) planes. The layered ruthenic acid compound has a layered crystal structure having a thickness of 1 nm or smaller.

[0013]

A first example of the layered ruthenic acid compound of the present invention is potassium ruthenate represented by the formula (2)



where $0 < x < 1$, $0 \leq n \leq 10$.

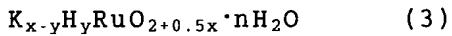
A first method for synthesizing the potassium ruthenate is a method of heating a potassium salt such as potassium carbonate or potassium hydroxide with ruthenium oxide at 700-900°C, preferably in an inert atmosphere.

A second synthesis method is a method of melting potassium hydroxide and ruthenium oxide at 500-700°C.

A third synthesis method is a method of dispersing a protonic ruthenic acid hydrate to be described later in an aqueous solution of potassium hydroxide or potassium chloride and stirring it.

[0014]

A second example of the layered ruthenic acid compound is a protonic ruthenic acid hydrate represented by the formula (3)

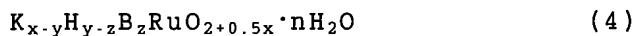


where $0 < x < 1$, $0 \leq y < x$, $0 \leq n \leq 10$.

The protonic ruthenic acid hydrate may be synthesized by subjecting a layered potassium ruthenate as a starting material to a proton exchange reaction in an acidic aqueous solution.

[0015]

A third example of the layered ruthenic acid compound is a layered alkylammonium-ruthenic acid intercalation compound represented by the formula (4). This is a compound in which alkylammonium is intercalated in the layered ruthenic acid compound.



where B is alkylammonium represented by $(R)_mNH_{4-m}$ or $(R)_{m-n}(R')_nNH_{4-m}$ (R and R' is $CH_3(CH_2)_p$, $m = 0$ to 4, $n = 0$ to 3, $p = 0$ to 18), $0 < x < 1$, $0 \leq y < x$, $0 \leq z < y$, $0 \leq n \leq 10$.

[0016]

By dispersing the layered alkylammonium-ruthenic acid

intercalation compound in a high dielectric solvent, nanosheets are isolated layer by layer in colloid form. By collecting them, the layered ruthenic acid compound which is porous and has excellent proton and electron conductivity is obtained.

The layered ruthenic acid compound according to the present invention can be applied to not only an electrochemical device but also an electrode for a polymer electrolyte fuel cell, a photocatalyst and a dye sensitizing photovoltaic cell.

[0017]

[Examples]

Hereinafter, the present invention is described in further detail by way of examples.

« Example 1 »

1. Preparation of layered potassium ruthenate:

A layered potassium ruthenate may be synthesized by a solid phase method or a melting method.

[0018]

(1) Synthesis by solid phase method

(a) K_2CO_3 and RuO_2 are mixed in the molar ratio of 1.25:1. (b) The resulting mixture is sintered under an inert gas flow such as Ar at 850 °C for 12 hours. (c) The sintered mixture is washed with distilled water to remove excess potassium. (d) A solid component is collected by filtration or centrifugation.

The molar ratio of K_2CO_3 to RuO_2 is preferably 1.1 to 1.5. Further, the sintering can be carried out in an atmospheric air, but the inert atmosphere such as Ar gas is preferable. The reaction temperature is preferably 700-900 °C.

[0019]

(2) Preparation by melting method

- (a) KOH and RuO_2 are mixed in the molar ratio of 3:1.
- (b) The resulting mixture is melted in air at 600 °C for 0.5 hours.
- (c) The melted mixture is washed with distilled water to remove excess potassium.
- (d) A solid component is collected by filtration or centrifugation.
- (e) A hydrate is obtained through air-drying, from which an anhydrate is obtained by drying at 120 °C.

The molar ratio of KOH and RuO_2 is preferably 2-3:1. The melting temperature is preferably 500-700 °C. The atmosphere may be air, but the inert atmosphere is preferable.

[0020]

(3) Preparation by ion exchange method

As an alternative method, the synthesis may be carried out by ion exchange of a protonic layered ruthenic acid hydrate described later. The synthesis steps are as follows.

- (a) A protonic layered ruthenic acid hydrate is dispersed in a KOH or KCl aqueous solution.
- (b) The dispersion is stirred at 60-80 °C.
- (c) The resulting compound is washed with distilled water to remove excess potassium.
- (d) A solid component was collected by filtration or

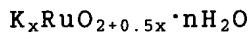
centrifugation. (e) A hydrate is obtained through air-drying, from which an anhydrate is obtained by drying at 120 °C.

[0021]

2. Physical properties of layered potassium ruthenate:

(1) Composition of layered potassium ruthenate

The layered potassium ruthenate is represented by the following formula:



where value x varies in the range of $0 < x < 1$ depending on the synthesis conditions. Water content n is $n = 0.4$ by drying at 120°C and varies in the range of $n = 0$ to 3 depending on the drying conditions. The optimum value of the water content is determined depending on the intended electrochemical device, but it is necessary to keep the falling rate-of-drying level.

[0022]

(2) Morphology of layered potassium ruthenate

FIGS. 1A and 1B show scanning electron microscopic images. Observed is a plate-like crystal of several hundred nm in length and width and several ten nm in thickness.

(3) Structure of layered potassium ruthenate

FIG. 2 shows a powder X-ray diffraction pattern. A layered structure having a basal interplanar spacing $d_{001} = 0.695$ nm is shown. Table 1 shows the diffraction peak indexing. In the X-ray diffraction pattern, peak intensities at other planes than (001) planes are too low to define their

indexes. FIG. 3A shows an electron diffraction pattern and FIG. 3B shows a transmission electron microscopic image. The ruthenium oxide layers each have a thickness of 1 nm or smaller and are regularly ordered in two-dimensional array.

[0023]

[Table 1]

$2\theta / {}^\circ$ (CuK α)	d/nm	h	k	l
12.74	0.695	0	0	1
25.54	0.349	0	0	2
38.72	0.233	0	0	3
52.44	0.174	0	0	4

[0024]

In the above results, potassium ruthenate is adopted as an example, but various alkali metals (Cs or the like) may also be applicable.

[0025]

« Example 2 »

1. Preparation of protonic layered ruthenic acid hydrate:

A protonic layered ruthenic acid hydrate may be synthesized by a proton exchange reaction using the layered potassium ruthenate as a starting material. The synthesis steps are as follows.

(a) The layered potassium ruthenate is stirred in diluted hydrochloric acid at 60 °C for 48 hours. (b) An excess of hydrochloric acid is washed away with distilled water. (c) A solid component is collected by filtration or centrifugation.

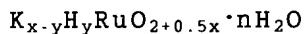
The acid used herein is not limited to hydrochloric

acid. The same result is obtained with use of sulfuric acid, nitric acid and hydrogen bromide. Time and temperature for the stirring also vary depending on the amount to be synthesized. Synthesis at room temperature is also possible, but the reaction time is prolonged.

[0026]

2. Physical properties of protonic layered ruthenic acid hydrate:

The protonic layered ruthenic acid hydrate comprises the following chemical composition



where $0 < x < 1$, $0 \leq y < x$, $0 \leq n \leq 10$.

Value y representing the amount of H varies depending on the conditions for the acid treatment. When the acid treatment is performed at 60°C for 48 hours, $x - y < 0.05$ is satisfied. Water content n satisfies $n = 0.4$ after drying at 120°C , which varies from $n = 0$ to 10 depending on the drying conditions.

3. Morphology of protonic layered ruthenic acid hydrate

FIGs. 4A and 4B show scanning electron microscopic images. Observed is a plate-like crystal of several hundred nm in length and width and several ten nm in thickness.

4. Structure of protonic layered ruthenic acid hydrate

FIG. 5 shows a powder X-ray diffraction pattern. A layered structure having a basal interplanar spacing $d_{001} = 0.457$ nm is shown. Table 2 shows the diffraction peak

indexing. In the X-ray diffraction pattern, peak intensities at other planes than (001) planes were too low to define their indexes.

[0029]

[Table 2]

$2\theta / {}^\circ$ (CuK α)	d/nm	h	k	l
19.46	0.456	0	0	1
39.34	0.229	0	0	2
60.94	0.152	0	0	3

[0030]

FIGS. 6A shows an electron diffraction image and FIG. 6B shows a transmission electron microscopic image. The ruthenium oxide layers each have a thickness of 1 nm or smaller and are regularly ordered in two-dimensional array. The ruthenium oxide layers are crystalline.

In the structure of the protonic layered ruthenic acid, ruthenium oxide layers having a thickness of 1 nm or smaller and hydrated water are regularly arranged in two-dimensional array. The surface of the ruthenium oxide layer is covered with a hydroxyl group to give a well crystalline structure. The degree of hydration is not particularly defined by the structure and the protonic layered ruthenic acid is able to contain water to such an extent that it almost reaches an infinite swelling state. In the existing amorphous hydrous oxide and electrolytically oxidized ruthenium hydrate, the arrangement of the ruthenium oxide and water is disordered and the water molecule exists in the gap of the structure.

Therefore, the degree of hydration is limited by the macrostructure to some extent.

[0031]

« Example 3 »

1. Preparation of layered alkylammonium-ruthenic acid intercalation compound:

A layered alkylammonium-ruthenic acid intercalation compound is obtained by an ion exchange reaction, a guest exchange reaction or an acid-base reaction. The synthesis steps are as follows.

(1) Synthesis by ion exchange reaction

(a) The protonic layered ruthenic acid hydrate is dispersed in an aqueous alkylammonium solution. (b) The solution is stirred at room temperature for 3 days. (c) Excess organic substance is washed away with distilled water. (d) A solid component is collected by filtration or centrifugation.

Alkylammonium used is $(R)_mNH_{4-m}$ or $(R)_{m-n}(R')_nNH_{4-m}$ (where R and R' are $CH_3(CH_2)_p$, m = 0 to 4, n = 0 to 3, p = 0 to 18).

[0032]

(2) Synthesis by acid-base reaction

(a) The protonic layered ruthenic acid hydrate is dispersed in an aqueous alkylamine solution. (b) The solution is stirred at room temperature for 3 days. (c) Excess organic substance is washed away with distilled water. (d) A solid component is collected by filtration or centrifugation.

Alkylamine used is $(R)_mNH_{3-m}$ or $(R)_{m-n}(R')_nNH_{3-m}$ (where R and R' are $CH_3(CH_2)_p$, m = 0 to 3, n = 0 to 2, p = 0 to 18).

[0033]

(3) Synthesis by guest exchange reaction

(a) A layered alkylammonium-ruthenic acid intercalation compound is dispersed in an aqueous alkylammonium solution. (b) The solution is stirred at room temperature for 3 days. (c) Excess organic substance is washed away with distilled water. (d) A solid component is collected by supercentrifugation.

Alkylammonium used is the same as that used in the above synthesis by the ion exchange reaction.

[0034]

2. Composition of layered alkylammonium-ruthenic acid intercalation compound:

The layered alkylammonium-ruthenic acid intercalation compound comprises the following composition:

$$H:alkylammonium:Ru = y-z:z:1 \text{ (molar ratio)}$$

where value x representing an organic substance content varies depending on the preparation conditions and the kind of alkyl chain, and $y < 1$.

[0035]

3. Morphology of layered alkylammonium-ruthenic acid intercalation compound:

FIG. 7 shows a scanning electron microscopic image of a layered cetyltrimethylammonium-ruthenic acid intercalation

compound. Observed is a stripe pattern at a spacing of about 2.8 nm. This is the basal interplanar spacing in the XRD described later.

[0036]

4. Structure of layered alkylammonium-ruthenic acid intercalation compound:

FIGs. 8, 9 and 10 show powder X-ray diffraction patterns of a layered ethylammonium-ruthenic acid intercalation compound, a layered tetrabutylammonium-ruthenic acid intercalation compound and a layered cetyltrimethylammonium-ruthenic acid intercalation compound, respectively. The compounds have layered structures having the basal interplanar spacing $d_{001} = 0.816$ nm, 1.68 nm and 2.76 nm, respectively. Tables 3, 4 and 5 show the diffraction peak indexes of these compounds.

[0037]

[Table 3]

$2\theta / {}^\circ$ (CuK α)	d/nm	h	k	l
10.86	0.815	0	0	1
21.72	0.409	0	0	2
32.92	0.272	0	0	3
44.38	0.204	0	0	4

[0038]

[Table 4]

$2\theta / {}^\circ$ (CuK α)	d/nm	h	k	l
5.22	1.693	0	0	1
10.46	0.846	0	0	2
15.82	0.560	0	0	3
21.22	0.419	0	0	4
26.66	0.334	0	0	5
32.16	0.278	0	0	6
37.76	0.238	0	0	7
43.56	0.208	0	0	8

[0039]

[Table 5]

$2\theta / {}^\circ$ (CuK α)	d/nm	h	k	l
3.22	2.742	0	0	1
6.48	1.364	0	0	2
9.69	0.913	0	0	3
12.88	0.688	0	0	4
15.99	0.554	0	0	5
19.32	0.460	0	0	6
22.50	0.395	0	0	7
25.75	0.346	0	0	8
28.80	0.310	0	0	9

[0040]

《 Example 4 》

1. Preparation of colloidal layered ruthenic acid nanosheet:

A colloidal layered ruthenic acid nanosheet is synthesized by dispersing a layered tetrabutylammonium-ruthenic acid intercalation compound in a solvent. The synthesis steps are as follows.

(a) The layered tetrabutylammonium-ruthenic acid intercalation compound is dispersed in a high dielectric

solvent. (b) The dispersion was stirred by ultrasonic treatment. (c) A colloid component (supernatant) is collected by centrifugation (2000 rpm).

As the high dielectric solvent, may be used water, methanol, isopropyl alcohol, acetonitrile, dimethylformamide, dimethyl sulfoxide, propylene carbonate and the like.

[0041]

2. Composition of colloidal layered ruthenic acid nanosheet:

The colloidal layered ruthenic acid nanosheet comprises the following composition
High dielectric solvent: tetrabutylammonium: layered ruthenic acid nanosheet = 100-x:0.075x:x (molar ratio)

where value x represents a concentration of the layered tetrabutylammonium-ruthenic acid intercalation compound, which is about 2 to 100 $\mu\text{g/L}$.

[0042]

3. Morphology of colloidal layered ruthenic acid nanosheet:

FIG. 11 shows a scanning electron microscopic image of the colloidal layered ruthenic acid nanosheet supported on carbon. Observed is an isolated crystalline nanosheet having a length and width of several hundred nm and a thickness of the nanometer order.

[0043]

4. Structure of colloidal layered ruthenic acid nanosheet (thin film of layered tetrabutylammonium-ruthenic acid intercalation compound):

By casting a dispersion containing the colloidal layered ruthenic acid nanosheets on a glass substrate, an oriented thin film of a layered tetrabutylammonium-ruthenic acid intercalation compound is obtained. FIG. 12 shows a powder X-ray diffraction pattern. The oriented thin film has a layered structure having the basal interplanar spacing $d_{001} = 1.68 \text{ nm}$ and excellent c-axis orientation. Table 6 shows the diffraction peak indexing.

[0044]

[Table 6]

$2\theta / {}^\circ (\text{CuK}\alpha)$	d/nm	h	k	l
5.22	1.693	0	0	1
10.46	0.846	0	0	2
15.82	0.560	0	0	3
21.22	0.419	0	0	4
26.66	0.334	0	0	5
32.16	0.278	0	0	6
37.76	0.238	0	0	7
43.56	0.208	0	0	8

[0045]

« Example 5 »

1. Fabrication of electrode for electrochemical supercapacitor using protonic layered ruthenic acid hydrate and capacitance of electrochemical capacitor:

The protonic layered ruthenic acid hydrate is dispersed in a solvent such as water or dimethylformamide (about 40 $\mu\text{g/L}$) and the resulting dispersion is dropped on a cross-sectional surface of a glassy carbon rod (5 mm in diameter). Further, a perfluorocarboxylic acid ionomer sold

under the trade name Nafion by DuPont was dropped thereon as a fixing agent and then dried to obtain a glassy carbon electrode supporting the protonic layered ruthenic acid hydrate (hereinafter abbreviated as HRO/GC). FIG. 13 shows cyclic voltammogram (CV) obtained by scanning at a scan rate of 500 to 2 mV/s in an electrolyte of 0.5 M sulfuric acid using the HRO/GC electrode, a counter electrode of platinum mesh and a reference electrode of Ag/AgCl. When the scanning is performed at a high rate, a square-like CV is obtained, which is a unique feature of the pseudo electrical double-layer capacitor. When the scanning is performed at a low rate, a redox capacitance resulted from the oxidation-reduction reaction is obtained in addition to a pseudo electrical double-layer capacitance. The capacitance derived from the pseudo electrical double-layer capacitor is hardly dependent on the scan rate, while the redox capacitance increases with a decrease in scan rate.

[0046]

Table 7 shows the capacitances of the HRO/GC electrode calculated from the CVs obtained at various scan rates. The capacitance slightly increases with a decrease in scan rate. This is caused by the above-mentioned increase of the redox capacitance. The obtained capacitance is similar to that of hydrous ruthenium oxide synthesized by electrolytic oxidation and an order of magnitude larger than that of rutile-type ruthenium oxide.

The pseudo electrical double-layer capacitance of ruthenium oxide is generally considered as about $80 \mu\text{F}/\text{cm}^2$ (microfarad/effective surface area). Using this, an active surface area is calculated as $410 \text{ m}^2/\text{g}$ from the capacitance at 50 mV/s (330 F/g). An effective surface area of conventional rutile-type ruthenium oxide is 50 to $60 \text{ m}^2/\text{g}$ even in a fine particle having a particle diameter of 10 nm (specific surface area obtained by BET method).

[0047]

[Table 7]

Scan Rate/ mV s^{-1}	Capacitance/ F g^{-1}	Electrochemical activity area/ $\text{m}^2 \text{ g}^{-1}$
0.2	375	469
0.5	363	454
2	352	440
5	347	434
20	337	421
50	330	413
200	319	399
500	301	376

[0048]

The protonic layered ruthenic acid hydrate has different characteristics from those of existing amorphous hydrous ruthenium oxide and rutile-type ruthenium oxide. The characteristics are listed below.

(i) The protonic layered ruthenic acid hydrate is extremely large in electrochemically active surface area. Each of the layers in the protonic layered ruthenic acid has a thickness of 1 nm or smaller and protons or hydrated protons can move

freely between the layers. The specific surface area becomes as large as 470 m²/g.

(ii) In the form of HRO/GC, a clear redox couple is observed when the charge/discharge is slow (the scan rate is low or the charge/discharge is performed at a small current). This component is dependent on a crystalline structure and cannot be obtained in the amorphous hydrous ruthenium oxide. The redox capacitance depends on the active surface area. In rutile-type crystalline ruthenium oxide, the redox capacitance is solely obtained on the particle surface, which is extremely less contributory. The active surface area of the rutile-type ruthenium oxide is 50 m²/g, whereas that of the protonic layered ruthenic acid is 470 m²/g, which is almost 10 times larger than that of the rutile-type ruthenium oxide. In the case of protonic layered ruthenic acid, the interlayer space itself is electrochemically active. Therefore, the redox capacitance that cannot be achieved in the rutile-type ruthenium oxide is obtained.

[0049]

(iii) In the HRO/GC, a certain capacitance is obtained even if the charge/discharge is extremely fast (the scan rate is high or the charge/discharge is performed at a large current). This capacitance includes a non-faradaic electrical double-layer capacitance component and a pseudo-faradaic capacitance component. These capacitance components are dependent on the electrochemically active surface area. In the rutile-type

ruthenium oxide, these capacitance components are extremely less contributory because they are obtained solely on the particle surface. The active surface area of the rutile-type ruthenium oxide is $50 \text{ m}^2/\text{g}$, whereas that of the protonic layered ruthenic acid is $470 \text{ m}^2/\text{g}$, which is almost 10 times larger than the above). Since the interlayer space itself in the protonic layered ruthenic acid is electrochemically active, a pseudo capacitance that cannot be achieved in the rutile-type ruthenium oxide is obtained.

[0050]

The protonic layered ruthenic acid allowed the electrolyte to permeate between the crystalline ruthenium oxide layers, giving proton conductivity without deteriorating the electron conductive network. Further, the thickness of the ruthenium oxide layers was reduced to as small as 0.5 nm or smaller, thereby attaining an active surface area as extremely large as $470 \text{ m}^2/\text{g}$. As a result, the non-faradaic electrical double-layer capacitance component and the pseudo-faradaic capacitance are obtained at very rapid speed on the layer surface, thereby a large capacitance is obtained even when the charge/discharge is performed at a large current. Moreover, since a redox capacitance derived from the crystalline structure is also obtained on the layer surface, a larger capacitance is obtained when the charge/discharge is performed at a low rate. Thus, the layered ruthenic acid hydrate is a large-capacitance electrochemical supercapacitor

material capable of rapid charging and discharging and exhibits extremely high energy density and power density.

[0051]

It is assumed that such high energy density and high power density are ascribable to excellent mixed proton/electron conductivity of the protonic layered ruthenic acid hydrate. In general, whether the mixed proton/electron conductivity is good or not can be judged on the analogy of i-V characteristic (CV). As the grounds for the above assumption, the i-V characteristic shows favorable rise even at a high scan rate, keeping the square form similar to that of a capacitor. Further, it is also judged from the absence of resistance. It is also understood from the numeric data shown in Tables 7 and 9, in which capacitance loss is hardly observed even if the scan rate is raised.

[0052]

For example, regarding the capacitance at 0.2 mV/s as 100%, the scan rate is raised. The capacitance loss of rutile-type RuO₂ and rutile-type (Ru, V) O₂ decreases by half at 500 mV/s, whereas the layered HRO decreases to 80 %. This suggests that the proton conductivity is maintained to a sufficient degree. Table 8 shows the data.

[0053]

[Table 8]

Scan rate/ MVs ⁻¹	Layered HRO/ Fg ⁻¹	Rutile-RuO ₂ / Fg ⁻¹	Rutile- (Ru _{0.5} V _{0.5})O ₂ / Fg ⁻¹
0.2	375(100)	46(100)	387(100)
0.5	363(97)	38(83)	321(83)
2	352(94)	32(70)	289(75)
5	347(93)	30(65)	282(73)
20	337(90)	27(59)	252(65)
50	330(88)	25(54)	236(61)
200	319(85)	23(50)	204(53)
500	301(80)	22(48)	186(48)

[0054]

« Example 7 »

An explanation is given of an example in which a layered ruthenic acid compound according to the present invention is applied to an electrochemical device. The layered ruthenic acid compound has an extremely stable crystalline structure as understood from the SEM image and the X-ray diffraction pattern. Hereinafter, steps of manufacturing the electrochemical device are described.

[0055]

(a) Pulverizing step: a layered ruthenic acid compound is pulverized roughly, and then finely, followed by classification into particles having a particle diameter of 8 to 2.5 μm .

(b) Mixing, kneading step: to 40 parts by weight of the classified layered ruthenic acid compound and 50 parts by weight of activated carbon powder (BP-20 manufactured by

KURARAY CHEMICAL, average particle diameter 5 μm , specific surface area 2200 m^2/g , average pore diameter 16 Å), are added 4 parts by weight of a conductive material, 2 parts by weight of a primary binder, 2 parts by weight of a permanent binder and 2 parts by weight of a rubber material. The mixture is subjected to dry blending, wet blending and kneading to prepare an electrode material.

[0056]

(c) Various electrode materials: as the conductive material, acetylene black and ketchen black are used in the ratio of 1:1 by weight. As the primary binder, starch and carboxymethyl cellulose are used in the ratio of 1:1 by weight. It is preferable to use, as the permanent binder, a sol of polytetrafluoroethylene (PTFE) when an aqueous solvent is used, or a sol of polyvinylidene fluoride (PVDF) when an organic solvent is used. As the rubber material, it is preferable to use NBR and SBR in the ratio of 1:1 by weight. As the activated carbon powder, usable are any of coconut shell activated carbon, phenol-based activated carbon, coal pitch-based activated carbon, petroleum pitch-based activated carbon and aerogel carbon.

[0057]

(d) Shaping step, drying step: depending on the shape and size of the electrochemical device, a press or a coater is used. The drying is performed at 100 °C or lower when an organic solvent is used. When an aqueous solvent is used,

water content is removed, the primary binder is burned away, the drying is performed to the falling rate-of-drying stage, a sheet of about 120 μm thick is formed using a roller and cut into a desired shape to obtain a sheet electrode. In the case of forming a coin-shaped capacitor, a pair of sheet electrodes are stacked with a separator (polyvinyl alcohol-based synthetic paper of 50 μm thick, manufactured by Nippon Kokan) interposed therebetween. To form a cylindrical capacitor, a pair of sheet electrodes sandwiching a separator therebetween are wound in a spiral fashion to form an electrochemical device.

(e) Housing: the above-mentioned device is housed into a coin-shaped or cylindrical case together with an electrolyte. Thus, the electrochemical device is completed.

(f) Evaluations: charge/discharge characteristics of the obtained electrochemical devices are evaluated at a discharge rate determined in view of actual use and a temperature of 85, 45, 25, 0 or -20°C.

[0058]

An electrochemical device using a conventional ruthenium compound contains ruthenium oxide, which is expensive. Therefore, the ruthenium oxide is in a thin film form and dispersed in an island pattern. Accordingly, even though the initial performance is excellent, the obtained electrochemical device causes exfoliation of ruthenium oxide from the activated carbon through repeated charge/discharge.

Therefore, the conventional electrochemical device has not been put into practical use. On the other hand, the layered ruthenic acid compound according to the present invention showed excellent crystallinity, which realized stable charge/discharge characteristics during long-term operation.

[0059]

« Example 8 »

Fabrication of electrode for electrochemical supercapacitor using a colloidal layered ruthenic acid nanosheet and the capacitance of the electrochemical capacitor:

Colloidal ruthenic acid nanosheets obtained by dispersing a layered tetrabutylammonium-ruthenic acid intercalation compound in a high dielectric solvent, in which each of the nanosheets is isolated (exfoliated) while maintaining its crystal structure, are dispersed in the dispersion solvent in a stable state to show a property similar to that of swelling clay. A solution containing the thus exfoliated ruthenic acid nanosheets is used to form an electrode of glassy carbon rod whose surface is modified with the ruthenic acid nanosheet in the same manner as the manufacture of the clay-modified electrode. More specifically, the solution containing the colloidal ruthenic acid nanosheets is dropped on the surface of the glassy carbon rod, followed by drying, and then the above-described perfluorocarboxylic acid ionomer is dropped thereon and dried to form the electrode. The obtained ruthenic acid nanosheet-modified

electrode is subjected to scanning at a scan rate of 50 mV/s under the same conditions described in Example 5 to obtain a CV, which is indicated by a in FIG. 14. As comparisons, FIG. 14 also shows CVs b and c of normal HRO (prototypic layered ruthenic acid hydrate) particles and rutile-type RuO₂ nanoparticles, both of which are not exfoliated. The CV curve is essentially similar to that obtained with use of the layered ruthenic acid hydrate. However, in the ruthenic acid nanosheet-modified electrode, a capacitance component derived from oxidation-reduction reaction is clearly observed even at a high scan rate, which means that the oxidation-reduction reaction becomes more contributory to the whole capacitance. In the ruthenic acid nanosheet-modified electrode, the colloidal ruthenic acid nanosheets form a disordered structure, decreasing diffusion resistance of protons and allowing smoother permeation of the electrolyte into the space between the layers.

[0060]

For these reasons, as seen in Table 9, use of the ruthenic acid nanosheet allows to obtain favorable supercapacitor characteristics even under charge/discharge at a high rate. Hence, the ruthenic acid nanosheet is more suitable for applications requiring high power and high energy than a layered ruthenic acid.

[0061]

[Table 9]

Scan rate/ MV s ⁻¹	Capacitance/ F/g ⁻¹)	Electrochemical activity area/ m ² /g ⁻¹
0.2	549	686
0.5	493	616
2	479	599
5	458	572
20	429	536
50	407	509
200	375	469
500	354	443

[0062]

« Example 9 »

A comparison with various capacitors is shown.

To make a comparison among a commercially available electrical double-layer capacitor using an activated carbon electrode, an electrochemical capacitor using rutile-type ruthenium oxide and electrochemical capacitors representative of the present invention, coin-shaped cells of 20 mm in diameter and 1.6 mm in thickness, respectively were assembled and their capacitances per unit volume and unit cubic capacity were measured. Table 10 shows the results. In the Table, Aqueous signifies acid electrolytes such as sulfuric acid, hydrochloric acid and perchloric acid, or alkaline electrolytes such as KOH, NaOH and LiOH. In this example, 8 N KOH aqueous solution was used. Capacitor I of the present invention was a capacitor using the electrode of Example 7, while capacitor II was a capacitor using the ruthenium acid nanosheet-modified electrode of Example 8. As seen in Table 10, the capacitors of the present invention showed the

capacitance per unit mass 8 to 11 times as large as that of the rutile-type capacitor and 2 to 3 times as large as that of the electrical double-layer capacitor. Further, the capacitance per unit volume was 5 to 8 times larger than that of the rutile-type capacitor and 9 to 12 times larger than that of the electrical double-layer capacitor.

[0063]

[Table 10]

	Electrolyte	m^2/g	F/g	F/cc
Activated carbon electrode	Organic	1800 - 2200	35 - 42	16 - 22
Rutile-type electrochemical capacitor	Aqueous	50 - 80	12	30
Present invention: Capacitor I	Aqueous	350	94	150
Present invention: Capacitor II	Aqueous	400	140	250

[0064]

[Effects of the Invention]

The present invention provides a layered ruthenic acid compound having a crystalline structure of 1 nm or smaller in thickness. The layered ruthenic acid compound is higher in charging capability than conventional ruthenium oxide, and hence it is effectively used as an electrode of an electrochemical device.

[BRIEF EXPLANATION OF THE DRAWINGS]

[FIG. 1A]

There is shown a scanning electron microscopic image

of a layered potassium ruthenate of the present invention.

[FIG. 1B]

There is shown an enlargement of the same scanning electron microscopic image.

[FIG. 2]

There is shown a powder X-ray diffraction pattern of the layered potassium ruthenate of the present invention.

[FIG. 3A]

There is shown an electron diffraction pattern of the layered potassium ruthenate of the present invention.

[FIG. 3B]

There is shown a transmission electron microscopic image of the layered potassium ruthenate of the present invention.

[FIG. 4A]

There is shown a scanning electron microscopic image of a protonic layered ruthenic acid hydrate of the present invention.

[FIG. 4B]

There is shown an enlargement of the scanning electron microscopic image.

[FIG. 5]

There is shown a powder X-ray diffraction pattern of the protonic layered ruthenic acid hydrate of the present invention.

[FIG. 6A]

There is shown an electron diffraction pattern of the protonic layered ruthenic acid hydrate of the present invention.

[FIG. 6B]

There is shown a transmission electron microscopic image of the protonic layered ruthenic acid hydrate of the present invention.

[FIG. 7]

There is shown a scanning electron microscopic image of a layered cetyltrimethylammonium-ruthenic acid intercalation compound of the present invention.

[FIG. 8]

There is shown a powder X-ray diffraction pattern of a layered ethylammonium-ruthenic acid intercalation compound of the present invention.

[FIG. 9]

There is shown a powder X-ray diffraction pattern of a layered tetrabutylammonium-ruthenic acid intercalation compound of the present invention.

[FIG. 10]

There is shown a powder X-ray diffraction pattern of the layered cetyltrimethylammonium-ruthenic acid intercalation compound of the present invention.

[FIG. 11]

There is shown a scanning electron microscopic image of a colloidal layered ruthenic acid nanosheet supported on

carbon according to the present invention.

[FIG. 12]

There is shown a powder X-ray diffraction pattern of the colloidal layered ruthenic acid nanosheet supported on carbon according to the present invention.

[FIG. 13]

There are shown cyclic voltammograms of an HRO/GC electrode of the present invention at a scan rate of 500 to 2 mV/s.

[FIG. 14]

There is shown a cyclic voltammogram of a ruthenic acid nanosheet-modified electrode of the present invention at a scan rate of 50 mV/s.

2003-092872

(Translation)

[DOCUMENT NAME] Abstract

[ABSTRACT]

[OBJECTIVE] to provide a layered ruthenic acid compound with increased active area.

[SOLVING MEANS] A layered ruthenic acid compound having high diffraction intensities at (001), (002), (003) and (004) planes, respectively, and having a layered crystalline structure with a thickness of 1 nm or smaller. A typical compound is a protonic ruthenic acid hydrate represented by the formula $K_{x-y}H_yRu_{02+0.5x} \cdot nRuO$.

[SELECTED DRAWING] FIG. 1B

[DOCUMENT NAME] Drawings

[FIG. 1A] [FIG. 1B]

[FIG. 2] intensity/cps

[FIG. 3A] [FIG. 3B] [FIG. 4A]

[FIG. 4B]

[FIG. 5] intensity/cps

[FIG. 6A] [FIG. 6B] [FIG. 7]

[FIG. 8] intensity/cps

[FIG. 9] intensity/cps

[FIG. 10] intensity/a.u.

[FIG. 11]

[FIG. 12] intensity/cps

[FIG. 13] [FIG. 14]